# Tailoring $N_2$ DBD for Controlled Monolayer Graphene Film Processing

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**Abstract:** This contribution examines the modification of graphene films by low-frequency $N_2$ Dielectric Barrier Discharge at atmospheric pressure. Distinct operating conditions are investigated, including diffuse (Townsend) and filamentary DBD regimes, and plasma-treated graphene is characterized by RIMA and XPS analysis. These studies highlight a number of fundamental features in plasma-graphene interactions, including the kinetics driving the nitrogen incorporation reaction, the unexpected self-healing of plasma-generated defects, and the role of local vs local energy deposition.

## 1. Introduction

Plasma processing shows promises for tailoring graphene's properties. Since graphene's discovery in 2004, numerous low-pressure plasmas have been explored for inducing defects or doping graphene. On the other hand, much less efforts have been devoted to atmospheric pressure plasmas. These methods have the potential to drive the scale-up of modified graphene production, much like how chemical vapor deposition (CVD) has facilitated the large-scale production of monolayer graphene.

In this work, graphene is exposed to a low-frequency Dielectric Barrier Discharge (DBD) characterized by a high density of atomic nitrogen and metastable species $N_2(A)$. First, the kinetics of defect generation and nitrogen incorporation are investigated. Subsequently, relaxation (or self-healing) mechanisms are explored to fine-tune defect formation and further control nitrogen incorporation. Lastly, the influence of localized microdischarges on the graphene structure is examined.

## 2. Experimental Details

A low-frequency (1 kHz) DBD in a plane-to-plane configuration is sustained with nitrogen gas $N_2$ at a flow rate of 2.14 L/min and a pressure of 750 Torr. High-quality CVD graphene on a $SiO_2$/Si substrate is positioned on the bottom alumina electrode, 1 mm below the upper alumina plate. To analyse the graphene samples after various treatments, Hyperspectral Raman Imaging (RIMA) and X-ray Photoelectron Spectroscopy (XPS) are used. Raman spectroscopy provides insights into graphene's structural properties, while RIMA enhances this analysis by offering spatial resolution and enabling statistical evaluation. The study is conducted in three phases. (i) *Time-Series Analysis*: A diffuse DBD discharge regime is used to treat the graphene for varying durations between 10 and 60 s. (ii) *Sub-Dose Experiments*: A 30 s treatment to the diffuse DBD regime is divided into multiple sub-doses, from a single 30 s exposure (1× 30 s) up to five shorter exposures (5× 6 s) with relaxation phases in between to examine the effects of intermittent treatments. (iii) *Filamentary Discharge Exposure*: Graphene is exposed to a filamentary discharge for either 30 s or 1 s to investigate the effects of localized energy deposition on its structure.

## 3. Results and Discussion

RIMA measurements of the time series for varying treatment durations reveal that defect density increases with extended treatment time. The evolution of the N/C ratio initially shows an increase before plateauing at approximately 5% for longer exposure times. This trend indicates that nitrogen incorporation is primarily governed by defect formation. However, a different behavior is observed during the relaxation phase under a constant total treatment time. In this case, a high N/C ratio is measured for low defect densities (as confirmed by RIMA analysis) and gradually decreases with increasing defect density, eventually stabilizing again at 5%. Additionally, graphene can be transformed into graphene nanosheets under the filamentary discharge regime. A single filament impact point was further isolated and characterized by RIMA measurements. This revealed a pronounced spatial gradient in defect density, underscoring the localized energy deposition effects of the filamentary DBD regime.

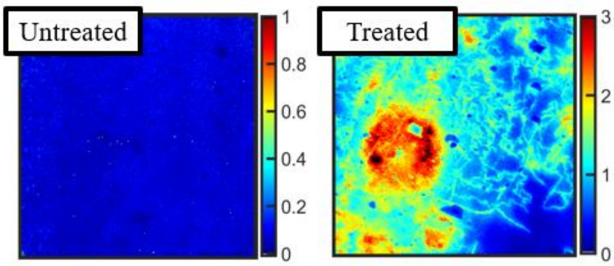


Figure 1: (130x130) μm² Raman mapping of the defect density for the untreated and treated sample exposed to 1 s filamentary discharge.

## 4. Conclusion

This contribution presents various processing methods for graphene in an atmospheric pressure DBD and their effects on the material's structural and chemical properties. Nitrogen incorporation can be precisely controlled by tailoring the processing parameters, such as exposure duration and relaxation phases. To induce local morphological changes, the filamentary regime proves to be more effective due to its localized energy deposition.